10.40 Thermodynamics **Fall 2003**
Problem Set 2

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2. You are asked to prove that $\Delta \underline{S}$ for an irreversible, adiabatic process is always > 0. Consider the following closed system cyclic process for an ideal gas.

I. An irreversible, adiabatic expansion from point 1at T_A , P_A to point 2 atT_B, P_B where $T_A > T_B$ *and* $P_A > P_B$.
II. A reversible, isothermal compression from point 2 to point 3 at T_B
III. A reversible, adiabatic compression from point 3 to point 1

(a) Assuming only *PdV* work, sketch a possible cyclic path for steps I –III on a *P*-*V* diagram.

(b) Using the exact differential, state function characteristics of $\underline{S}$ prove that $\Delta \underline{S}$ for step I is always > 0 for an ideal gas expanding adiabatically and irreversibly from point 1at T_A ,P_A to point 2 at T_B,P_B

(c) Is $\Delta \underline{S}$ for step I > 0 for a non-ideal gas as well? Explain your answer.

Be sure to state and justify all assumptions made

SOLUTION

Part A) Your solution should look similar to the plot shown below from the given information in the problem statement.

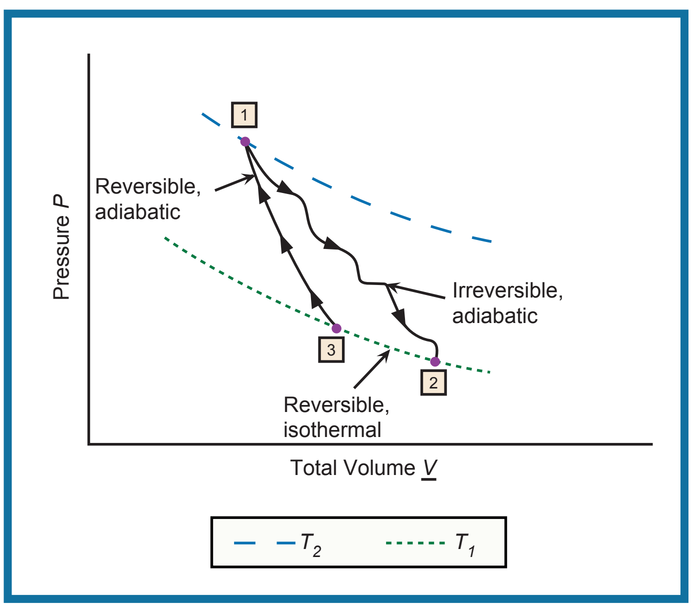

Image by MIT OCW.

Part B)
Assumptions:
Ideal gas
Closed system
Only PdV work

Solution:
To solve this problem, examine the entropy balance for the entire closed loop path.

$$\oint d\underline{S} = 0 = \sum \Delta\underline{S}_{ij} = \Delta\underline{S}_{12} + \Delta\underline{S}_{23} + \Delta\underline{S}_{31}$$

Examine the two reversible pathways:

For path 3-1, we know that the path is reversible and adiabatic. Thus,

$$\Delta\underline{S}_{31} = \int \frac{\delta Q_{rev}}{T} = 0$$

For path 2-3, we know that this path is reversible and isothermal. Thus,

$$\Delta\underline{S}_{23} = \int \frac{\delta Q_{rev}}{T_B} = \frac{Q_{rev,23}}{T_B}$$

And from the First Law:

$$\Delta\underline{U}_{23} = Q_{23} + W_{23} = NC_v\Delta T = 0$$

$$Q_{rev,23} = -W_{23} = \int_2^3 PdV < 0 \qquad \text{or} \qquad \Delta\underline{S}_{23} = \frac{Q_{rev,23}}{T_B} < 0$$

Where $Q_{rev}<0$ because it is an isothermal compression and $\Delta S_{23}<0$ because T_B is positive.

With these substitutions,

$$\Delta\underline{S}_{12} = -\Delta\underline{S}_{23} \qquad \boxed{\Delta\underline{S}_{12} > 0}$$

Part C) Show that $\Delta S_{12}>0$ for non-ideal gas as well.

For this part, the solution is similar to the analysis above.

$$\oint d\underline{S} = 0 = \sum \Delta\underline{S}_{ij} = \Delta\underline{S}_{12} + \Delta\underline{S}_{23} + \Delta\underline{S}_{31}$$

$$\Delta\underline{S}_{31} = \int \frac{\delta Q_{rev}}{T} = 0$$

We know that path 3-1 is reversible and adiabatic.

$$\Delta\underline{S}_{23} = \int \frac{\delta Q_{rev}}{T_A} = \frac{Q_{rev,23}}{T_A}$$

We know that path 2-3 is isothermal and reversible.
However, when we do the first law analysis on this system, we must account for the non-ideal gas. Here, we do a first law balance on the entire pathway since we know that the change in internal energy for the entire cycle must be zero.

$$\oint d\underline{U} = 0 = \Delta\underline{U} = Q_{rev,12} + Q_{rev,23} + Q_{rev,31} + \sum W_{ij}$$

We know that $Q_{rev,12}$ and $Q_{rev,31}$ are zero because they are adiabatic pathways. This results in the following equation.

$$W_{net} = -Q_{rev,23}$$

From the entropy balance, we get that

$$\Delta\underline{S}_{12} = \frac{-Q_{rev,23}}{T_A} = \frac{-Q_{net}}{T_A}$$

We want to conclude that $\Delta S_{12}>0$. Let's see what happens if Q_{net} is greater than or equal to zero, which would disprove our hypothesis that $\Delta S_{12}>0$.

If $Q_{net}=0$, then the overall cycle is adiabatic. This is not true because $Q_{23}\neq 0$.

If $Q_{net}>0$, then the net effect of the cycle is to transfer Q_{23} into the system and produce the same amount of work in the surroundings ($W_{net}=-Q_{rev,23}$). This is a clear violation of the Kelvin-Planck statement of the second law. It would also violate Postulate II, since it produces a PMM2. This case is the equivalent of case 4 on page 69 of the textbook, which was proved to be invalid.

Thus, the final answer is:

$$Q_{net} = Q_{rev,23} < 0 \qquad\qquad \Delta\underline{S}_{12} > 0$$